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Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 3144707 C 2023/01/24

(11)(21) 3 144 707

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2021/01/11
(87) Date publication PCT/PCT Publication Date: 2021/07/22
(45) Date de délivrance/Issue Date: 2023/01/24
(85) Entrée phase nationale/National Entry: 2022/01/18
(86) N° demande PCT/PCT Application No.: US 2021/012940
(87) N° publication PCT/PCT Publication No.: 2021/146135
(30) Priorités/Priorities: 2020/01/13 (US16/741,225); 2020/02/21 (US16/797,686)

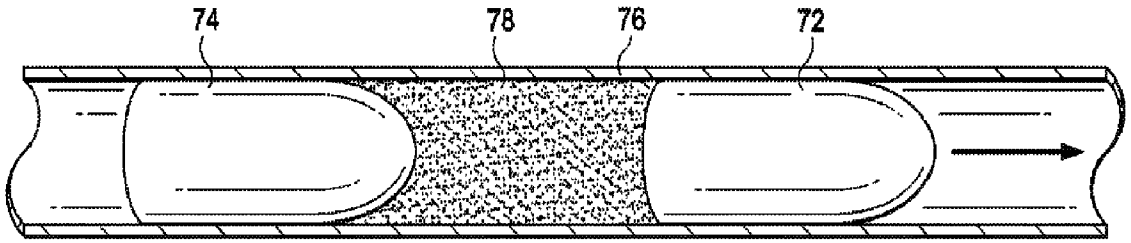
(51) Cl.Int./Int.Cl. *B08B 9/02* (2006.01), *B08B 9/027* (2006.01), *B08B 9/04* (2006.01)

(72) Inventeur/Inventor:
ALLRED, JR. JAMES A., US

(73) Propriétaire/Owner:
RIDDLE'S DEHI & CHEMICAL SERVICES CO., LLC
D/B/A E&P SERVICES GROUP, US

(74) Agent: KIRBY EADES GALE BAKER

(54) Titre : PROCEDE DE NETTOYAGE DE PIPELINE
(54) Title: METHOD OF CLEANING PIPELINE



(57) Abrégé/Abstract:
A method of cleaning a pipeline is performed by introducing a treatment composition comprising a colloidal particle dispersion having inorganic nanoparticles with an average particle size of from 500 nm or less into an interior of a pipeline to be cleaned. A pig or body is passed through the pipeline to spread the composition upon surfaces of the interior of the pipeline. The composition and materials adhering to the surfaces of the interior of the pipeline are removed to facilitate cleaning of the pipeline.

Date Submitted: 2022/01/18

CA App. No.: 3144707

Abstract:

A method of cleaning a pipeline is performed by introducing a treatment composition comprising a colloidal particle dispersion having inorganic nanoparticles with an average particle size of from 500 nm or less into an interior of a pipeline to be cleaned. A pig or body is passed through the pipeline to spread the composition upon surfaces of the interior of the pipeline. The composition and materials adhering to the surfaces of the interior of the pipeline are removed to facilitate cleaning of the pipeline.

METHOD OF CLEANING PIPELINE

TECHNICAL FIELD

[0001] The invention relates to methods of cleaning pipelines using particular treatment compositions.

BACKGROUND

[0002] Pipelines are used throughout the world to efficiently and economically transport large quantities of fluids over great distances. Some of these pipelines may be hundreds and sometimes thousands of miles in length, particularly those used to transport crude and refined petroleum oil, natural gas, chemicals, etc. Over time, the interior surfaces of the pipeline can become coated with deposits that can restrict and eventually block flow. These deposits may include corrosion byproducts, scale, mineral deposits, sand, silica, hydrocarbons, paraffins, asphaltenes, metal oxides, iron oxides, solids, biofilm, and water.

[0003] Pipelines used for these fluids are typically formed from metals, such as carbon steel. While the exterior of the pipelines is typically painted or covered with a protective coating to prevent corrosion, the interior of the pipelines are typically unprotected or bare metal so that they are subject to corrosion. Cathodic corrosion protection, where a small electrical current is applied to the pipeline so that it becomes cathodic, can offer some protection against internal pipe corrosion, but this does not prevent all corrosion.

[0004] Additionally, the deposits that form on the interior surfaces of the pipeline can form corrosion cells in which under-deposit corrosion can occur. Such corrosion cells require the presence of water in the pipeline, which forms the electrolyte in the corrosion cell. This water is typically present in the pipeline as entrained water within the transported fluids. Fluids that are conveyed through pipelines typically contain some water. Even dry natural gas has some amount of water (e.g., 4-7 lbs water/MMSCF of gas or 0.064-0.112 kg water/1000 SCM gas) that allows the formation of corrosion cells. The water can penetrate these surface deposits becoming entrapped under the deposit to form the corrosion cell and facilitate the under-deposit corrosion.

[0005] There are various sources of these corrosion causing materials. This can include carbon dioxide (CO_2) and hydrogen sulfide (H_2S) that may be present in the transported fluids. Carbon dioxide hydrates in the presence of water to form carbonic acid (H_2CO_3). The acid in turns reacts with the iron or steel to form corrosion. The hydrogen sulfide also reacts with the iron

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or steel material of the pipeline to form iron sulfides, thus corroding and degrading the pipe. These materials can penetrate the surface deposits to form the corrosion cells.

[0006] Microbiologically influenced corrosion (MIC) from microbes or bacteria that may be present in the fluids is also a source of corrosion. These microbes or bacteria may attach to the internal surfaces of the pipeline or under the surface deposits and grow as a colony to form a biofilm on the surfaces of the pipe. These microbes are often present in fluids produced from subterranean formations, such as oil and gas wells. The microbes are typically chemoautotrophs, which obtain energy by the oxidation of electron donors from their surroundings. One type of such microbes are sulfate-reducing bacteria (SRB). SRBs utilize sulfate ions (SO_4^{2-}) that are reduced to H_2S. Water within the pipeline will interact with the metal surfaces to create a layer of molecular hydrogen. The SRBs through anaerobic respiration will then utilize the sulfate ions so that the hydrogen layer on the walls of the pipeline is oxidized to H_2S, which in turns reacts with iron to form iron sulfides. Another type of MIC that leads to corrosion in pipelines is that produced by acid producing bacteria (APB). ABPs undergo anaerobic fermentation instead of anaerobic respiration, producing acids as part of their growth cycle. These produced acids lead to the acid corrosion of the metal materials of the pipeline.

[0007] To remove these deposits, coatings, and other detrimental materials, a maintenance program is carried out. This essentially involves passing a projectile, commonly referred to as a "pig," down the interior of the pipeline so that the deposits are physically scraped off the sides of the pipeline as the pig is moved through the pipeline. This process, referred to as "pigging" is sometimes done in conjunction with a chemical treatment. Pigging treatments are usually conducted "on-line" without interfering with the transporting of fluids. While such treatments have been used with limited success, improvements are needed.

SUMMARY

[0007a] Certain exemplary embodiments provide a method of cleaning a pipeline comprising: selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline; introducing a treatment composition comprising the colloidal particle dispersion and a drying agent into an interior of the pipeline; allowing the composition to act upon materials adhering to the surfaces of the interior of the pipeline to loosen and break up the materials adhering to the surfaces of the interior of the pipeline; and removing the loosened and broken materials from the pipeline.

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[0007b] Other exemplary embodiments provide a method of cleaning a pipeline comprising: selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion to facilitate penetration of solid deposits on interior surfaces of the pipeline by the nanoparticles; introducing a treatment composition comprising the colloidal particle dispersion into an interior of the pipeline to be cleaned; passing a pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline; and removing the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline.

[0007c] Yet other exemplary embodiments provide a method of cleaning a gas or liquid petroleum pipeline comprising: selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline; introducing a treatment composition comprising the colloidal particle dispersion into an interior of the pipeline having a diameter of 24 inches or more; allowing the composition to act upon materials adhering to the surfaces of the interior of the pipeline to loosen and break up the materials adhering to the surfaces of the interior of the pipeline; and removing the loosened and broken materials from the pipeline.

[0007d] Still yet other exemplary embodiments provide a method of cleaning gas or liquid petroleum pipeline comprising: selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of from 300 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline; introducing a treatment composition comprising the colloidal particle dispersion, a surfactant, and a drying agent into an interior of the pipeline to be cleaned; passing a first pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline at a thickness of from 0.1 mil to 10 mils; and performing at least one of A) and B), wherein: A) comprises removing the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline with the same first pig or body as the first pig or body passes through the pipeline; and B) comprises allowing the composition to reside upon the surfaces of the interior of the pipeline for a selected period of time of 10 minutes or more; and then passing a second pig or body through the pipeline to remove the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline; and wherein the removed materials comprise at least one of corrosion byproducts, scale, mineral deposits, sand, silica, hydrocarbons, paraffins, asphaltenes, metal oxides, iron oxides, solids, biofilm, and water.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0008] For a more complete understanding of particular embodiments of the invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying figures, in which:

[0009] FIG. 1 is a schematic of a pipeline and pipeline segment having a pig launcher and receiver for passing a pig through the pipe to facilitate cleaning of the pipeline;

[0010] FIG. 2 is a schematic of a pipeline segment showing a single pig and pill of the treatment composition being passed through the pipeline segment; and

[0011] FIG. 3 is a schematic of a pipeline segment showing a dual pig and pill of the treatment composition being passed through the pipeline segment.

DETAILED DESCRIPTION

[0012] The present invention involves a method of cleaning a pipeline wherein a particular treatment composition is used in combination with one or more pigging operations. Referring to FIG. 1, a schematic of an exemplary pipeline 10 having a pipeline segment 12 is shown to illustrate the treatment method. The pipeline 10 may be any pipeline used for gathering, conveying and transporting fluids where the interior of the pipeline may require routine or periodic cleaning and maintenance. This may include pipelines used for gathering and/or transporting hydrocarbons, such as crude and refined petroleum oil, natural gas, natural gas liquids (NGS), chemicals, bio-oils, biofuels, etc. The pipeline may also be used to transport water or other aqueous fluids in certain instances. The pipeline 10 and/or pipeline segment 12 may be of varying lengths, from several feet (meters) to many miles (kilometers).

[0013] The pipe and components of the pipeline are typically formed of metal materials. These may include iron, aluminum, copper, metal alloys, and the like. In most applications, the pipelines or portions thereof are formed from iron or steel, such as carbon steel, mild or low carbon steel, cast iron, stainless steel, etc. In some instances, non-metal materials may also be used for the pipelines or portions thereof. These may include materials such as clay, plastic or polymeric materials, PVC, polypropylene, fiberglass, etc. For pipelines used for transporting natural gas and petroleum products, the pipelines are typically constructed from carbon steel.

[0014] The pipe of the pipeline or pipeline segment may be of various widths or diameters, from a fraction of an inch or a few inches to several feet (e.g., from 1/4 in to 5 ft or more or from 0.5 cm to 2 meters or more) in diameter. For pipelines used for transmission of fluids

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over great distances, such as natural gas and petroleum products, the pipelines are typically quite large in diameter (e.g., from 24 inches to 42 inches or from 0.5 meter to 1.5 meters).

[0015] The pipeline 10 may be divided into a number of different pipeline sections or segments 12 along its length. The pipeline segments 12 facilitate maintenance, operation and inspection of portions of the pipeline 10. The pipe segment 12 may have a uniform diameter along its length. Each segment 12, which may itself be several hundred feet to many miles in length, may be provided with a pig launcher assembly 14 at one end and a pig receiver assembly 16 at an opposite end. The launcher and receiver assemblies 14, 16 shown and described herein are exemplary of those commonly used in pipelines. Variations of these assemblies may also be used.

[0016] The pig launcher assembly 14 is located at an upstream end of the pipe segment 12 relative to the direction of fluid flow within the pipeline. Similarly, the pig receiver assembly 16 is located on a downstream end of the pipe segment 12. The launcher assembly 14 has an enlarged or major barrel or pipe portion 18 with opening at the end of the barrel 18 for accessing the interior of the barrel 18. An access door or closure 20 is provided for selectively accessing and closing off the end opening of the barrel 18. This also allows for the introduction of a pig or body 22 as well as other items or materials into the barrel 18.

[0017] The pig or body 22 may have a variety of configurations and constructions depending on its purpose. These can include mandrel pigs, foam pigs, solid cast pigs, etc. In the treatment methods disclosed herein, at least one pig or body is sized and configured to apply, spread or coat a treatment composition on the interior surfaces of the pipeline. Such pigs or bodies may have a reduced diameter or diameter portion to facilitate spreading of the treatment composition so that it is spread generally around the entire circumference of the pipe interior and so that the treatment composition stays in place upon the pipeline walls, without being scraped or otherwise readily removed by the pig or body. The size of the spreader pig or body may be of a selected diameter or size so that in combination with the amount of treatment composition introduced into the pipeline, the treatment composition may be applied at a selected thickness along the length of the pipe segment 12.

[0018] In certain embodiments, a single pig or body 22 may be used to both apply the treatment composition as well as remove deposits or materials from the surfaces of the pipeline simultaneously. In such instances, the pig or body 22 may have downstream features or portions configured to facilitate applying the treatment composition and upstream features or portions configured for removing deposits or materials from the surfaces of the pipeline.

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[0019] In other embodiments of the treatment, at least one pig or body 22 is a cleaner or scraper pig that is used for removing deposits or materials from the surfaces of the pipeline after a first pig is used to apply the treatment composition. In some applications, scraper pigs or bodies 22 of different sizes or diameters may be used that are successively introduced into the pipeline, from smaller to larger, so that deposits are removed progressively as the size of the pig increases.

[0020] One or more final drying pigs may also be used in certain embodiments to facilitate drying the pipeline after the cleaning or scraping operation is carried out.

[0021] The launcher assembly 14 further includes a reducer portion 24 that tapers to a smaller minor barrel portion 26 upstream from a pig trap valve 28, which is coupled to a mainline 30 of the line segment 12. The trap valve 28 is used to selectively open and close off communication between the launcher assembly 14 and the mainline 30 of the pipeline segment 12 and allows the passage of the pig 22 from the minor barrel portion 26 to the mainline 30, which may be of the same or similar diameters.

[0022] A kicker line 32 fluidly couples the major barrel portion 18 to a bypass inlet line 34. The bypass inlet line 34 is used to introduce fluid flow from the upstream pipeline 10 into the mainline 30 of the pipeline segment 12. The kicker line 32 diverts fluid flow from the bypass line 34 to the barrel 18. The kicker line 32 may couple to the barrel 18 as far upstream as possible to facilitate launching of the pig or body 22. A trap bypass valve 36 of the kicker line 32 is used to control fluid flow from bypass line 34. A bypass valve 38 is also provided for selectively controlling fluid flow through bypass line 34 to mainline 30.

[0023] A balance line 40 is shown fluidly coupled to the kicker line 32 and the minor barrel portion 26 near the trap valve 28. The balance line 40 is used to balance the pressure on both sides of the pig 22 when it is located within the major barrel portion 18 to minimize or prevent movement of the pig 22 within the launcher assembly 14. A control valve 42 allows the balance line 40 to be selectively opened or closed.

[0024] Other valves and lines (not shown), such as for venting, purging, injecting, draining fluids, etc., may also be coupled to the launcher assembly 14 and its components to facilitate various functioning of the launcher assembly 14. For example, with both the trap valve 28 and trap bypass valve 38 closed, the barrel 18 may be vented to atmospheric pressure to allow the door 20 to be opened and allowing the pig 22 to be introduced and positioned within the launcher 14.

[0025] With the door 20 closed and the pig 22 located within the launcher 14, the trap bypass valve 36 and pig trap valve 28 can be opened and the bypass valve 38 and balance valve 42

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can be closed. This causes fluid flow through the bypass line 34 to be directed through the kicker line 32 to the major barrel portion 18. The pig 22 is thereby forced out of the launch assembly 14 so that it is directed downstream down the mainline 30 of pipeline segment 12.

[0026] When the pig 22 passes the trap valve 28, the bypass valve 38 can be opened and the trap bypass valve 36 and pig trap valve 28 can be closed. Fluid flow from bypass line 34 through mainline 30 will continue to force the pig 22 downstream down the length of the line segment 12 to the receiver pig assembly 16.

[0027] The receiver assembly 16 is configured similarly to the launcher assembly 16. Like the launcher assembly 16, the receiver assembly includes a major barrel portion 44 and access door or closure 46 for selectively closing the end opening of the barrel portion 44. A tapered reducer portion 48 fluidly couples the major barrel portion 44 to a reduced diameter minor barrel portion 50 upstream from the major barrel portion 44. The minor barrel portion 50 is located downstream from a pig trap valve 52, which is coupled to the downstream end of the mainline portion 30 of the line segment 12. The trap valve 52 is used to selectively open and close off communication between the receiver assembly 16 and the mainline portion 30 of the pipeline segment 12 and allows the passage of the pig 22 from the mainline portion 30 to the minor barrel portion 50, which may be of the same or similar diameters

[0028] A return line 54 fluidly couples the major barrel 44 to the bypass outlet line 56. The bypass outlet line 56 directs fluids downstream to the remainder of the pipeline 10. The return line 54 returns fluid flow from the barrel 44 to the bypass outlet line 56. The return line 54 typically couples to the barrel 44 at position near the reducer 48. A trap bypass valve 58 of the return line 54 is used to selectively return fluid flow from barrel 44 through the return line 54 to the bypass outlet line 56. A bypass valve 60 is also provided for controlling fluid flow through bypass line 34 from mainline 30.

[0029] A balance line 62 is shown fluidly coupled to the return line 54 and the minor barrel portion 50 near the trap valve 52. The balance line 62 is used to balance the pressure on both sides of the pig 22 when it is located within the major barrel portion 44 to minimize or prevent movement of the pig 22 within the receiver assembly 14. A control valve 64 allows the balance line 62 to be selectively opened or closed.

[0030] Other valves and lines (not shown), such as for venting, purging, injecting, draining fluids, etc., may also be coupled to the receiver assembly 16 to facilitate various functioning of the receiver assembly 16.

[0031] By opening trap valve 52 and trap bypass valve 58, the pig 22 can be received within the receiver assembly 16. The bypass valve 60 can be closed or partially closed to facilitate

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directing the pig 22 into the barrel portion 44. When the pig 22 is received within the major barrel portion 44 of the receiver assembly 16, the bypass valve 60 can be fully opened and the trap valve 52 and trap bypass valve 58 closed. The receiver assembly 16 can then be vented to atmospheric pressure and drained so that the access door 46 can be opened and the pig 22, along with any collected material or debris, can removed from the receiver assembly 16.

[0032] In this manner, treatments can be carried out without interrupting fluid flow through the pipeline. The pigs are passed through the pipeline utilizing the normal pipeline fluid flow and pressure. This is important on major pipelines where disruption in fluid flow (e.g., natural gas) can have significant negative consequences, such as natural gas used fuel to power plants, etc.

[0033] FIG 2. illustrates the movement of a spreader pig 66 down through the interior of pipeline segment 68 to be cleaned, which may the same or similar to the pipeline segment 12 of FIG. 1, previously described. The spreader pig 66 may be launched and received through launching and receiving assemblies, which may be the same or similar to those assemblies 14, 16 of FIG. 1 previously described. As shown in FIG. 2, a quantity of cleaning or treatment composition 70, which is described in more detail later, in the form of a mass or "pill" is introduced into the pipeline segment 68 ahead of the pig 66. The pig 66 facilitates spreading composition upon surfaces of the interior of the pipeline segment 68 along all or a portion of the length of the segment 68.

[0034] FIG. 3 shows another embodiment wherein two pigs 72, 74 are used in pipeline segment 76. Here, pig 72 constitutes a lead pig and pig 74 constitutes a trailing pig. In this embodiment, a mass or pill 78 of treatment composition is introduced between the pigs 72, 74. The pigs 72, 74 facilitate spreading the treatment composition upon surfaces of the interior of the pipeline segment 68 along all or a portion of the length of the segment 76.

[0035] The amount of treatment composition used may be selected to provide a desired thickness applied to the walls of a pipeline segment along all or a portion of the length of the pipeline segment. This may be determined by the formula of Equation 1 below:

$$V = \pi \cdot [(R^2 - (R-T)^2] \cdot L \qquad (1)$$

where V is the total volume of treatment composition used, R is the internal radius of the pipe being treated, T is the desired thickness of the treatment composition to be applied to the walls of the pipe, and L is the length of the pipe being treated.

[0036] The treatment composition used for cleaning pipelines in accordance with the invention incorporates a colloidal particle dispersion having inorganic nanoparticles. In many cases the

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inorganic nanoparticles are silica nanoparticles, although other non-silica inorganic nanoparticles can be used alone or with silica nanoparticles. Colloidal silica dispersions using silica nanoparticles have been around for some time. They are typically formed from silica particles that are dispersed in a liquid phase. The liquid phase may be an aqueous or non-aqueous liquid or a combination of such liquids. The nanoparticles are stabilized electrostatically in the liquid so that they tend to stay suspended within the liquid. Non-limiting examples of various colloidal particle dispersions are those described in U.S. Patent Nos. 7,544,726 and 7,553,888 and U.S. Pat. App. Pub. Nos. US2016/0017204; US2018/0291255; US 2018/0291261; US2019/0078015; US2019/0078015; US2019/0136123; US2019/0225871, including the colloidal particle dispersions and compositions disclosed therein and the methods of making the same. Such colloidal particle dispersions are commercially available. Examples of suitable commercially available colloidal particle dispersions include, but are not limited to, those available from Nissan Chemical America Corporation as nanoActive®, nanoActive® HRT, nanoActive® EFT, and nanoActive® HNP solutions.

[0037] The inorganic nanoparticles of the colloidal particle dispersion will typically have particle size to facilitate formation of the colloidal particle dispersion so that the suspension remains stable. In many instances the inorganic nanoparticles will have an average particle size of from 500 nm or less. More often they will have an average particle size of from 300 nm or less, and still more particularly from 200 nm or less. In some embodiments, the inorganic nanoparticles will have an average particle size of from 0.1 nm to 500 nm, more particularly from 0.1 nm, 1 nm, 2 nm, 3 nm, 4nm, or 5 nm to 30 nm, 40 nm, 50 nm, 100 nm, 200 nm, or 300 nm. In certain applications the inorganic nanoparticles may have an average particle size of from at least, equal to, and/or between any two of 0.1 nm, 0.2 nm, 0.3 nm, 0.4 nm, 0.5 nm, 0.6 nm, 0.7 nm, 0.8 nm, 0.9 nm, 1 nm, 2 nm, 3 nm, 4 nm, 5 nm, 6 nm, 7 nm, 8 nm, 9 nm, 10 nm, 11 nm, 12 nm, 13 nm, 14 nm, 15 nm, 16 nm, 17 nm, 18 nm, 19 nm, 20 nm, 21 nm, 22 nm, 23 nm, 24 nm, 25 nm, 26 nm, 27 nm, 28 nm, 29 nm, 30 nm, 31 nm, 32 nm, 33 nm, 34 nm, 35 nm, 36 nm, 37 nm, 38 nm, 39 nm, 40 nm, 41 nm, 42 nm, 43 nm, 44 nm, 45 nm, 46 nm, 47 nm, 48 nm, 49 nm, 50 nm, 51 nm, 52 nm, 53 nm, 54 nm, 55 nm, 56 nm, 57 nm, 58 nm, 59 nm, 60 nm, 61 nm, 62 nm, 63 nm, 64 nm, 65 nm, 66 nm, 67 nm, 68 nm, 69 nm, 70 nm, 71 nm, 72 nm, 73 nm, 74 nm, 75 nm, 76 nm, 77 nm, 78 nm, 79 nm, 80 nm, 81 nm, 82 nm, 83 nm, 84 nm, 85 nm, 86 nm, 87 nm, 88 nm, 89 nm, 90 nm, 91 nm, 92 nm, 93 nm, 94 nm, 95 nm, 96 nm, 97 nm, 98 nm, 99 nm, 100 nm, 110 nm, 120 nm, 130 nm, 140 nm, 150 nm, 160 nm, 170 nm, 180 nm, 190 nm, 200 nm, 210 nm, 220 nm, 230 nm, 240 nm, 250 nm, 260 nm, 270 nm, 280 nm, 290 nm, 300 nm, 310 nm, 320 nm, 330 nm, 340 nm, 350 nm, 360 nm, 370 nm, 380 nm, 390 nm,

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400 nm, 410 nm, 420 nm, 430 nm, 440 nm, 450 nm, 460 nm, 470 nm, 480 nm, 490 nm, and 500 nm.

[0038] It should be noted in the description, if a numerical value, concentration or range is presented, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the description, it should be understood that an amount range listed or described as being useful, suitable, or the like, is intended that any and every value within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific points within the range, or even no point within the range, are explicitly identified or referred to, it is to be understood that the inventor appreciates and understands that any and all points within the range are to be considered to have been specified, and that inventor possesses the entire range and all points within the range, including smaller ranges within the larger ranges.

[0039] The inorganic nanoparticles, which are typically silica nanoparticles, may be surface functionalized with hydrophilic monomers and/or a mixture of hydrophilic and hydrophobic monomers. Such surface treatment can make the nanoparticles more stable in high saline or other disruptive conditions. Such surface treatment may be achieved with the use of silane compounds. Organosilanes are particularly useful for such surface modification. The colloidal inorganic nanoparticles can be surface modified by the reaction of colloidal silica surfaces with at least one moiety selected from the group consisting of a monomeric hydrophilic organosilane, a mixture of monomeric hydrophilic and monomeric hydrophobic organosilanes, or a polysiloxane oligomer.

[0040] Suitable monomeric hydrophilic organosilanes include, but are not limited to, glycidoxypropyl trimethoxysilane, glycidoxypropyl triethoxysilane, glycidoxypropyl tributoxysilane, glycidoxypropyl trichlorosilane, phenyl trimethoxysilane, phenyl trimethoxysilane, phenyl trichlorosilane, and combinations of these.

[0041] Suitable monomeric hydrophobic organosilanes include, but are not limited to, trimethoxy[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]silane, triethoxy[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]silane, trichloro[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]silane, methacryloxypropyl trimethoxysilane, methacryloxypropyl triethoxysilane, methacryloxypropyl trichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane, isobutyltrimethoxysilane, isobutyltriethoxysilane, isobutyltrichlorosilane, hexamethyldisiloxane, hexamethyldisilazane. and combinations of these.

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[0042] Suitable polysiloxane oligomers may include, but are not limited to, glycidoxypropyltrimethoxysilane, methacryloxypropyltrimethoxysilane, isobutyltrimethoxysilane, vinyltrimethoxysilane, trimethoxy[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyltrimethoxysilane, and hexamethyldisiloxane, and combinations of these.

[0043] In some instances, the inorganic nanoparticles may be encapsulated in a surfactant. Such encapsulation and surfactants are described, for instance, in U.S. Pat. App. Pub. No. US2016/0017204.

[0044] In the treatment composition, the amount of nanoparticles in the treatment composition may range from 60 wt.%, 50 wt.%, 40 wt.%, 30 wt.% or less by total weight of the treatment composition. In certain instances, the amount of particles will range from 0.001 wt.%, 0.01 wt.%%, 0.1 wt.%, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% to 10 wt.%, 15 wt.% to 30 wt.%, 35 wt.%, 40 wt.%, 45 wt.%, 50 wt.%, and 60 wt.% by total weight of the colloidal particle dispersion. In certain applications the inorganic nanoparticles may make up from at least, equal to, and/or between any two of 0.001 wt.%, 0.002 wt.%, 0.003 wt.%, 0.004 wt.%, 0.005 wt.%, 0.006 wt.%, 0.007 wt.%, 0.008 wt.%, 0.009 wt.%, 0.01 wt.%, 0.02 wt.%, 0.03 wt.%, 0.04 wt.%, 0.05 wt.%, 0.06 wt.%, 0.07 wt.%, 0.08 wt.%, 0.09 wt.%, 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%, 41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, 50 wt.%, 51 wt.%, 52 wt.%, 53 wt.%, 54 wt.%, 55 wt.%, 56 wt.%, 57 wt.%, 58 wt.%, 59 wt.%, and 60 wt.% by total weight of the colloidal particle dispersion.

[0045] The treatment composition further includes a solvent. This may be the solvent that the inorganic nanoparticles, which may be surface-functionalized nanoparticles, of the colloidal dispersion are initially dispersed in. The solvent may comprise water or aqueous liquids and/or non-aqueous liquids. In some embodiments, the solvent is an aqueous solvent that includes a mixture of water and alcohols. The alcohol solvent may be a C_1 to C_6 alcohol, such as methanol, ethanol, isopropyl alcohol, etc. The proportion of water to alcohol may range from

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100:1 to 1:100 by weight. Organic solvents may also be used alone or in combination with water. Organic solvents may include alcohols, methyl ethyl ketone (MEK), methyl isobutyl ketone, toluene, xylene, cyclohexane, dimethyl acetamide, ethyl acetate, etc. Combinations of various solvents, aqueous and non-aqueous, may be used.

[0046] The solvents may be present in the treatment composition in an amount of from 50 wt.% or less by total weight of the treatment composition. In particular embodiments, the solvent is present in the treatment composition in an amount of from at least, equal to, and/or between any two of 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%, 41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, and 50 wt.% by total weight of the treatment composition.

[0047] The treatment composition may also include a surfactant component. The surfactant may include an amphoteric surfactant, an ionic surfactant, an anionic surfactant, a cationic surfactant, a nonionic surfactant, or a combination of these. In particular embodiments, the surfactant is primarily an anionic surfactant with or without the use of a minor portion of non-ionic surfactants. Examples of suitable surfactants include, but are not limited to, ethoxylated nonyl phenol, sodium stearate, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, alkyl olefin sulfonates, laurylamine hydrochloride, trimethyldodecylammonium chloride, cetyl trimethylammonium chloride, polyethylene oxide alcohol, ethoxylated castor oil, propoxylated castor oil, ethoxylated-propoxylated castor oil, ethoxylated soybean oil, propoxylated soybean oil, ethoxylated-propoxylated soybean oil, ethylene oxide-propylene oxide copolymers, sodium trideceth sulfate, ethoxylated tetramethyl decyne alcohol, alkylphenolethoxylate, Polysorbate 80, ethoxylated or propoxylated polydimethylsiloxane, dodecyl betaine, lauramidopropyl betaine, cocamidopropyl betaine, cocamidopyropyl-2-hydroxypropyl sulfobetaine, alkyl aryl sulfonates, protein-surfactant complexes, fluorosurfactants, polyethyleneoxide alkyl ether phosphates, and combinations of these. In certain embodiments,

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the surfactant may be an ethylene oxide/propylene oxide copolymer, such as that available from AksoNobel as ETHYLAN 1206. An alkyl olefin sulfanate may also be used as the surfactant, such as that commercially available from Pilot Chemical as Calsoft® AOS-40. A suitable commercially available amphoteric surfactant is that available from Solvay as Mackam® CBS-50G.

[0048] The surfactants may be present in the treatment composition in an amount of from 0.01 wt.% to 50 wt.% by total weight of the treatment composition, more particularly from 0.1 wt.% to 10 wt.%, and still more particularly from 0.5 wt.% to 5 wt.%. In certain embodiments, the surfactants may be present in the treatment composition in an amount of at least, equal to, and/or between any two of 0.01 wt.%, 0.02 wt.%, 0.03 wt.%, 0.04 wt.%, 0.05 wt.%, 0.06 wt.%, 0.07 wt.%, 0.08 wt.%, 0.09 wt.%, 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%, 41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, and 50 wt.% by total weight of the treatment composition.

[0049] The treatment composition further include glycols. The glycols may act as solvent as well as act as a drying agent. Examples of such materials include, but are not limited to, ethylene glycol, propylene glycol, triethylene glycol, ethylene glycol mono n-propyl ether, propylene glycol methyl ether acetate, etc., and combinations of these. In many applications, the glycols will be ethylene glycol and triethylene glycol.

[0050] The glycols may be present in the treatment composition in an amount of from 50 wt.% or less by total weight of the treatment composition. In particular embodiments, the glycols may be present in the treatment composition of from 0.1 wt.% to 50 wt.%. In certain embodiments, the glycols may be present in the treatment composition in an amount of at least, equal to, and/or between any two of 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4

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wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%, 41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, and 50 wt.% by total weight of the treatment composition.

[0051] The treatment composition may also include a terpene and/or a terpenoid. Terpenes are organic compounds that are typically derived biosynthetically from units of isoprene, which has the molecular formula C_5H_8. The basic molecular formula of terpenes are multiples of this (i.e., $(C_5H_8)_n$ where n is the number of linked isoprene units). The isoprene units may be linked together "head to tail" to form linear chains or they may be arranged to form rings. Terpenoids are like terpenes but typically contain additional functional groups, such as oxygen or OH groups. One common example of a terpene compound is limonene. Limonene is a cyclic terpene. The d-isomer version of limonene is d-limonene, which is commonly available. Less common is the l-isomer, i.e., l-limonene. These and other terpene and terpenoid compounds are commercially available.

[0052] The terpene and/or terpenoid compounds may be present in the treatment composition in an amount of from 50 wt.% or less by total weight of the treatment composition. In particular embodiments, the terpene and/or terpenoid compounds may be present in the treatment composition in an amount of from 0 wt.% to 50 wt.%. In certain embodiments, the terpene and/or terpenoid compounds may be present in the treatment composition in an amount of at least, equal to, and/or between any two of 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%,

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41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, and 50 wt.% by total weight of the treatment composition.

[0053] In certain embodiments, the treatment composition includes a non-terpene oil. An example of a suitable non-terpene oil is methyl soyate. Methly soyate is a methyl ether derived from soybeans and methanol. The non-terpene oil may be present in the treatment composition in an amount of from 50 wt.% or less by total weight of the treatment composition. the non-terpene oil may be present in the treatment composition in an amount of from 0 wt.% to 50 wt.%. In certain embodiments, the non-terpene oil may be present in the treatment composition in an amount of at least, equal to, and/or between any two of 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5 wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, 5.0 wt.%, 5.5 wt.%, 6.0 wt.%, 6.5 wt.%, 7.5 wt.%, 8.0 wt.%, 8.5 wt.%, 9.0 wt.%, 9.5 wt.%, 10 wt.%, 11 wt.%, 12 wt.%, 13 wt.%, 14 wt.%, 15 wt.%, 16 wt.%, 17 wt.%, 18 wt.%, 19 wt.%, 20 wt.%, 21 wt.%, 22 wt.%, 23 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, 30 wt.%, 31 wt.%, 32 wt.%, 33 wt.%, 34 wt.%, 35 wt.%, 36 wt.%, 37 wt.%, 38 wt.%, 39 wt.%, 40 wt.%, 41 wt.%, 42 wt.%, 43 wt.%, 44 wt.%, 45 wt.%, 46 wt.%, 47 wt.%, 48 wt.%, 49 wt.%, and 50 wt.% by total weight of the treatment composition.

[0054] The treatment composition may further include a bio- or bacteria-reducing agent and/or biocide. A "biocide" is a technical definition that is defined by the EPA. In some instances, a bio-reducing or bacteria-reducing agent that does not meet the EPA definition of a biocide may be used. The difference may be the result of the concentrations and/or materials used. One non-limiting example of a suitable bacteria-reducing agent is glutaraldehyde. The bio- or bacteria-reducing agent and/or biocide may be used in an amount of from 0.01 wt.% to 5 wt.% by total weight of the treatment composition. In particular applications, the amount of bio- or bacteria-reducing agent and/or biocide may be at least, equal to, and/or between any two of 0.01 wt.%, 0.02 wt.%, 0.03 wt.%, 0.04 wt.%, 0.05 wt.%, 0.06 wt.%, 0.07 wt.%, 0.08 wt.%, 0.09 wt.%, 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2.0 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3.0 wt.%, 3.1 wt.%, 3.2 wt.%, 3.3 wt.%, 3.4 wt.%, 3.5 wt.%, 3.6 wt.%, 3.7 wt.%, 3.8 wt.%, 3.9 wt.%, 4.0 wt.%, 4.1 wt.%, 4.2 wt.%, 4.3 wt.%, 4.4 wt.%, 4.5

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wt.%, 4.6 wt.%, 4.7 wt.%, 4.8 wt.%, 4.9 wt.%, and 5.0 wt.% by total weight of the treatment composition.

[0055] A pH adjusting agent may also be used in the treatment composition. These may be acidic or alkali materials used to lower or raise the pH of the treatment composition to a selected level. The pH of the treatment composition may vary (e.g., a pH from 6 to 8) depending upon the composition makeup, the treatment to be performed and the purpose or fluids transported through the pipeline. In certain applications, the pH of the treatment composition will range from 6 to 7.

[0056] In certain embodiments the treatment composition may be free of or contain less than 0.1 wt.%, 0.01 wt.%, or 0.001 wt.% of any one or more of an iron chelator, tetrakis(hydroxymethyl)phosphonium chloride (THPC), tetrakis(hydroxymethyl)phosphonium sulfate (THPS), methanol, and/or ethanol. In the case of methanol, this may be avoided in those cleaning treatments used to clean pipelines for natural gas as it may mask the odors of mercaptans, which are used as odorants in natural gas to facilitate gas-leak detection.

[0057] In carrying out the treatment method for cleaning a pipeline, the treatment composition as has been described is introduced into an interior of a pipeline to be cleaned. Referring to FIG. 1, this will typically be at the upstream end of the pipeline segment 12, at or within the barrel portions 18, 20 of the pig launcher 14. The treatment composition may be introduced into the launcher through a port and valve formed for such purpose or may be introduced into the opening of the barrel portion 18. The treatment composition may also be injected at one or more positions spaced apart along the length of the pipeline segment 12. Injection ports (not shown) may be provided along the length of the pipeline segment 12 for this purpose.

[0058] The pig 22, which represents a spreader pig for applying the treatment composition to the surfaces of the interior of the pipeline, is introduced into the launcher 14 and/or pipeline segment 12, with the treatment composition located downstream of the pig 22. The spreader pig 22 can then be launched down the pipeline segment 12 so that it spreads the treatment composition along the walls of the interior of the mainline pipe 30 of pipeline segment 12.

[0059] In particular embodiments, the volume amount of treatment composition used may be that selected to provide a particular thickness according to Equation 1. The thickness of the treatment composition may vary. In many applications the thickness of the treatment composition applied to the walls of the treated pipe may range from 0.1 mil or 10 mils (0.0025 mm to 0.254 mm) or more. In particular embodiments, the treatment composition is applied to the walls of the treated pipe at a thickness at least, equal to, and/or between any two of 0.1

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mil (0.0025mm), 0.2 mil (0.0031 mm), 0.3 mil (0.0076 mm), 0.4 mil (0.0102 mm), 0.5 mil 0.0127 mm), 0.6 mil (0.0152 mm), 0.7 mil (0.0177 mm), 0.8 mil (0.0203 mm), 0.9 mil (0.0229 mm), 1.0 mil (0.0254 mm), 1.1 mils (0.0279 mm), 1.2 mils (0.0305 mm), 1.3 mils (0.0330 mm), 1.4 mils (0.0356 mm), 1.5 mils (0.0381 mm), 1.6 mils (0.0406 mm), 1.7 mils (0.0432 mm), 1.8 mils (0.0457 mm), 1.9 mils (0.0483 mm), 2.0 mils (0.0508 mm), 2.1 mils (0.0533 mm), 2.2 mils (0.0558 mm), 2.3 mils (0.0584 mm), 2.4 mils (0.0610 mm), 2.5 mils (0.0635 mm), 2.6 mils (0.0660 mm), 2.7 mils (0.0686 mm), 2.8 mils (0.0711 mm), 2.9 mils (0.0737 mm), 3.0 mils (0.0762 mm), 3.1 mils (0.0787 mm), 3.2 mils (0.0813 mm), 3.3 mils (0.0838 mm), 3.4 mils (0.0864 mm), 3.5 mils (0.0889 mm), 3.6 mils (0.0914 mm), 3.7 mils (0.0940 mm), 3.8 mils (0.0965 mm), 3.9 mils (0.0991 mm), 4.0 mils (0.1016 mm), 4.1 mils (0.1041 mm), 4.2 mils (0.1067 mm), 4.3 mils (0.1092 mm), 4.4 mils (0.1118 mm), 4.5 mils (0.1143 mm), 4.6 mils (0.1168 mm), 4.7 mils (0.1194 mm), 4.8 mils (0.1219 mm), 4.9 mils (0.1245 mm), 5.0 mils (0.1270 mm), 5.1 mils (0.1295 mm), 5.2 mils (0.1321 mm), 5.3 mils (0.1346 mm), 5.4 mils (0.1371 mm), 5.5 mils (0.1397 mm), 5.6 mils (0.1422 mm), 5.7 mils (0.1448 mm), 5.8 mils (0.1473 mm), 5.9 mils (0.1499 mm), 6.0 mils (0.1524 mm), 6.1 mils (0.1549 mm), 6.2 mils (0.1575 mm), 6.3 mils (0.1600 mm), 6.4 mils (0.1626 mm), 6.5 mils (0.1651 mm), 6.6 mils (0.1676 mm), 6.7 mils (0.1702 mm), 6.8 mils (0.1727 mm), 6.9 mils (0.1753 mm), 7.0 mils (0.1778 mm), 7.1 mils (0.1803 mm), 7.2 mils (0.1829 mm), 7.3 mils (0.1854 mm), 7.4 mils (0.1880 mm), 7.5 mils (0.1905 mm), 7.6 mils (0.1930 mm), 7.7 mils (0.1956 mm), 7.8 mils (0.1981 mm), 7.9 mils (0.2007 mm), 8.0 mils (0.2032 mm), 8.1 mils (0.2057 mm), 8.2 mils (0.2083 mm), 8.3 mils (0.2108 mm), 8.4 mils (0.2134 mm), 8.5 mils (0.2159 mm), 8.6 mils (0.2184 mm), 8.7 mils (0.2210 mm), 8.8 mils (0.2235 mm), 8.9 mils (0.2261 mm), 9.0 mils (0.2286 mm), 9.1 mils (0.2311 mm), 9.2 mils (0.2337 mm), 9.3 mils (0.2362 mm), 9.4 mils (0.2388 mm), 9.5 mils (0.2413 mm), 9.6 mils (0.2438 mm), 9.7 mils (0.2464 mm), 9.8 mils (0.2489 mm), 9.9 mils (0.2515 mm), and 10 mils (0.2540 mm).

[0060] As shown in FIG. 2, the treatment composition may be applied as a pill 70 before a single spreader pig 66. Alternatively, the treatment composition may be applied as a pill 78 between leading and trailing pigs 72, 74, as shown in FIG. 3. The passage of the pigs through the pipeline may result in both the application of treatment composition and removal of previously deposited materials simultaneously in certain instances.

[0061] In some embodiments, a single pig is used to both apply the treatment composition as well as remove the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline. In such situations, the treatment composition may only reside on the surfaces of the pipeline for a brief duration of a few seconds to even a

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fraction of a second depending upon the speed of the pig. This may sometimes be referred to as a "flush and brush" application, wherein the same pig is used to both apply or spread the treatment composition while also simultaneously removing materials as the pig body is passed through the pipeline.

[0062] In other embodiments, the treatment composition is applied to the walls of the pipeline with one pig or body that does not facilitate the removal of the applied treatment composition and those materials adhering to the walls of the pipeline. In such instances, the applied treatment composition is allowed to reside upon the surfaces of the interior of the pipeline for a period of time after it is applied without further passing a second cleaning or scraper pig through the pipeline. This may sometimes be referred to as a "soak and brush" application. The residence time that the treatment composition is allowed to reside on the walls of the pipeline after its application may range from 10 minutes or more. The residence time may vary depending upon the cleaning job to be performed. In many instances, the residence time may range from 10 minutes to several days, more particularly from 1 hr to 48 hrs, and still more particularly from 3 hrs to 24 hours. In particular embodiments, the treatment composition is allowed to reside on the walls of the pipeline from at least, equal to, and/or between any two of 10 min, 20 min, 30 min, 40 min, 50 min, 1 hr, 2 hrs, 3 hrs, 4 hrs, 5 hrs, 6 hrs, 7 hrs, 8 hrs, 9 hrs, 10 hrs, 11 hrs, 12 hrs, 13 hrs, 14 hrs, 15 hrs, 16 hrs, 17 hrs, 18 hrs, 19 hrs, 20 hrs, 21 hrs, 22 hrs, 23 hrs, 24 hrs, 25 hrs, 26 hrs, 27 hrs, 28 hrs, 29 hrs, 30 hrs, 31 hrs, 32 hrs, 33 hrs, 34 hrs, 35 hrs, 36 hrs, 37 hrs, 38 hrs, 39 hrs, 40 hrs, 41 hrs, 42 hrs, 43 hrs, 44 hrs, 45 hrs, 46 hrs, 47 hrs, and 48 hrs.

[0063] The treatment composition incorporating the inorganic nanoparticles provides a cleaning fluid that works to penetrate deposits on the interior surface of the pipeline by a Brownian-motion, diffusion-driven mechanism known as disjoining pressure. Moreover, depending upon the treatment composition makeup, the nanoparticles themselves may be charged. For example, the colloidal particle dispersion may be an anionic or a cationic colloidal silica dispersion. This may result in the nanoparticles being attracted to the material of the pipeline, such as pipelines that are provided with cathodic corrosion protection. This attraction, as well as the Brownian-motion, causes the nanoparticle materials to penetrate the deposits on the walls of the pipe to facilitate loosening and breaking up of the deposits that are formed on the interior surfaces of the pipeline.

[0064] After the selected residence time is reached, a cleaning or scraper pig may be passed through the pipeline to remove the treatment composition and those materials adhering to the

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surfaces of the interior of the pipeline. One or more cleaning or scraper pigs may be used for this purpose.

[0065] In certain instances, the process is repeated wherein the same or a different treatment composition is applied to the interior surfaces of the pipeline, followed by scraping or cleaning with the same or a different pig. For example, in a single pipeline segment, the treatment composition application/scraping cycle may be performed from 1 to 20 times or more. Different size pigs may be used for subsequent treatment/cleaning cycles. The amount of treatment composition applied during each cycle may be the same or vary from cycle to cycle.

[0066] One of the advantages of the treatment composition and method is that it dries water or moisture from the pipeline. While there can be some water used in the treatment composition, this water is not free water that will elevate the moisture content within the pipeline. This is because the water complexes with the other components (e.g., glycols) of the treatment composition. The drying agents further aid to absorb existing liquid water and vapor in the pipeline so that the treatment facilitates drying of the pipeline. As a result, in certain instances, a drying pig may not be necessary after the treatment has been carried out. In other applications, a drying pig may be passed through the pipeline to remove any residual water moisture or liquids.

[0067] In some applications, a corrosion inhibitor may be applied to the interior surfaces of the pipeline after the treatment composition and materials adhering to the surfaces of the interior of the pipeline are removed. Those corrosion inhibitors and application methods that are well known in the art may be used

[0068] The following examples serve to further illustrate various embodiments and applications.

EXAMPLES

EXAMPLE 1

[0069] A cleaning treatment was performed on an existing 84-mile-long (135 km), 36-inch (0.91 m) diameter dry gas line segment. This line was transferring 800 MMCF (22.6 MCM) of dry gas per day. The treatment composition was comprised of a colloidal particle dispersion having silica nanoparticles with an average particle size of from 500 nm or less, a glycol, and glutaraldehyde. The pipeline was cleaned at night because of lower gas demands than during daylight hours. During the treatment operation, valves that were feeding customers from the pipeline were closed. As the pig and treatment composition travelled down the pipeline, these valves were opened after passage of the pig downstream.

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[0070] Five different injection points for introducing the treatment composition were used along the length of the pipeline, each injection point being located approximately 15 miles to 20 miles (24 km to 32 km) apart. A treatment composition pill was sized to provide approximately 3 mils (0.0762 mm) coverage of the treatment composition on the walls of the pipe. The first injection of treatment composition was performed approximately 1 hour prior to the pig launch. The remaining injections at each injection point were made after the first injection, one hour prior to the arrival of the pig at the injection point.

[0071] The pig was a steel mandrel pig with discs and brushes that was speed controlled due to the high velocity of the gas to provide proper cleaning. The project called for a "flush and brush" application, wherein the pig was used to both apply or spread the treatment composition while also removing materials as the pig was passed through the pipeline. This process is effective but may not be as effective as a "soak and brush" application, wherein the treatment is allowed to reside on the walls of the pipeline for a period of time before removal.

[0072] The procedure was repeated five additional times. The same pig configuration was used on each run. The treatments were successful in removing 16,000 pounds (7257 kg) of solids during the cleaning operation in addition to the removed treatment composition. The treatments also reduced the dew point to a point less than that measured prior to the cleaning run.

EXAMPLE 2

[0073] A cleaning treatment was performed on a 46-mile-long (74 km), 30-inch (0.762 meter) diameter dry gas line segment. This line was transferring 130 MMCF (3.7 MCM) of dry gas per day. There were no customer gas feeds on the pipeline so that the treatment was carried out during daylight hours and without closing any customer feed valves. The need for a speed control pig was also not necessary for the cleaning project.

[0074] The cleaning procedure for the project was a "soak and brush" application. Two injection points were used on the pipeline. The first injection point was located just downstream from the pig launcher. The second was located approximately halfway between the pig launcher and the pig receiver. The treatment composition pill size was configured to provide approximately 5 mils (0.1270 mm) of coverage per run. The treatment composition was comprised of a colloidal particle dispersion having silica nanoparticles with an average particle size of from 500 nm or less, a glycol, and glutaraldehyde. The treatment composition was injected approximately one hour prior to the pig launch. A bullet-nose, poly-foam, channel pig was used to spread the treatment composition along the interior surfaces of the pipeline.

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The second injection of treatment composition was made one hour prior to the arrival of the pig at the injection point. The treatment composition spread on the interior surfaces of the pipeline was allowed to reside overnight.

[0075] The next day, a mandrel style, disc and brush pig was then launched in the pipeline to remove the chemical and debris from the pipeline. The treatment composition application/removal process was repeated four additional times. After it was determined that the line was cleaned, approximately 20,000 pounds (9071 kg) of solids was removed from the pipeline in addition to the removed treatment composition.

[0076] While the invention has been shown in some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes and modifications without departing from the scope of the invention. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the invention.

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CLAIMS

1. A method of cleaning a pipeline comprising:

selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline;

introducing a treatment composition comprising the colloidal particle dispersion and a drying agent into an interior of the pipeline;

allowing the composition to act upon materials adhering to the surfaces of the interior of the pipeline to loosen and break up the materials adhering to the surfaces of the interior of the pipeline; and

removing the loosened and broken materials from the pipeline.

2. The method of claim 1, further comprising:

passing a pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline.

3. A method of cleaning a pipeline comprising:

selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion to facilitate penetration of solid deposits on interior surfaces of the pipeline by the nanoparticles;

introducing a treatment composition comprising the colloidal particle dispersion into an interior of the pipeline to be cleaned;

passing a pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline; and

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removing the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline.

4. The method of claim 3, wherein:

the composition is allowed to reside upon the surfaces of the interior of the pipeline for a selected period of time; and wherein

removing the composition and materials adhering to the surfaces of the interior of the pipeline comprises passing a second pig or body through the pipeline to remove the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline.

5. The method of any one of claims 1 or 3, wherein:

the inorganic particles are silica nanoparticles.

6. The method of claim 5, wherein:

the silica nanoparticles are functionalized with hydrophilic monomers and/or a mixture of hydrophilic and hydrophobic monomers.

7. The method of any one of claims 1 or 3, wherein:

inorganic nanoparticles have an average particle size of 300 nm or less.

8. The method of any one of claims 1 or 3, wherein:

the inorganic nanoparticles have an average particle size of from 0.1 nm to 300 nm.

9. The method of any one of claims 1 or 3, wherein:

the pipeline comprises at least one of a gas pipeline and a liquid petroleum pipeline.

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10. The method of any one of claims 1 or 3, wherein:

the composition is spread upon surfaces of the interior of the pipeline in a thickness of from 0.1 mil to 10 mils.

11. The method of any one of claims 1 or 4, wherein:

the composition is allowed to reside upon the surfaces of the interior of the pipeline for 10 minutes or more.

12. The method of any one of claims 1 or 3, wherein:

the treatment composition has a pH of from 6 to 7.

13. The method of any one of claims 1 or 3, wherein:

the removed materials comprise at least one of corrosion byproducts, scale, mineral deposits, sand, silica, hydrocarbons, paraffins, asphaltenes, metal oxides, iron oxides, solids, biofilm, and water.

14. The method of any one of claims 1 or 3, wherein:

the inorganic nanoparticles are present in the treatment composition in an amount of from 0.001 wt.% to 60 wt.% by total weight of the treatment composition.

15. The method of any one of claims 1 or 3, wherein:

the inorganic nanoparticles are present in the treatment composition in an amount of from 0.01 wt.% to 10 wt.% inorganic nanoparticles by total weight of the treatment composition.

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16. The method of any one of claims 1 or 3, further comprising:

applying a corrosion inhibitor to the interior surfaces of the pipeline after the composition and materials adhering to the surfaces of the interior of the pipeline are removed.

17. The method of any one of claims 1 or 3, wherein:

the treatment composition further comprises at least one of a surfactant, an amphoteric surfactant, an ionic surfactant, an anionic surfactant, a cationic surfactant, a nonionic surfactant, a glycol, triethylene glycol, propylene glycol, ethylene glycol, glutaraldehyde, a bacteria-reducing agent, a biocide, a pH adjuster, water, an alcohol, a solvent, a dispersant, a non-terpene oil-based moiety, a terpene, a terpenoid, and limonine.

18. The method of any one of claims 1 or 3, wherein:

the treatment composition is free of any tetrakis(hydroxymethyl)phosphonium chloride (THPC), tetrakis(hydroxymethyl)phosphonium sulfate (THPS), methanol and ethanol.

19. A method of cleaning a gas or liquid petroleum pipeline comprising:

selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of 500 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline;

introducing a treatment composition comprising the colloidal particle dispersion into an interior of the pipeline having a diameter of 24 inches or more;

allowing the composition to act upon materials adhering to the surfaces of the interior of the pipeline to loosen and break up the materials adhering to the surfaces of the interior of the pipeline; and

removing the loosened and broken materials from the pipeline.

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20. A method of cleaning gas or liquid petroleum pipeline comprising:

selecting a colloidal particle dispersion having inorganic nanoparticles with an average particle size of from 300 nm or less that exhibit properties of Brownian motion that facilitate penetration of solid deposits on interior surfaces of the pipeline;

introducing a treatment composition comprising the colloidal particle dispersion, a surfactant, and a drying agent into an interior of the pipeline to be cleaned;

passing a first pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline at a thickness of from 0.1 mil to 10 mils; and

performing at least one of A) and B), wherein:

A) comprises removing the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline with the same first pig or body as the first pig or body passes through the pipeline; and

B) comprises allowing the composition to reside upon the surfaces of the interior of the pipeline for a selected period of time of 10 minutes or more; and then passing a second pig or body through the pipeline to remove the composition and materials adhering to the surfaces of the interior of the pipeline to facilitate cleaning of the pipeline; and wherein

the removed materials comprise at least one of corrosion byproducts, scale, mineral deposits, sand, silica, hydrocarbons, paraffins, asphaltenes, metal oxides, iron oxides, solids, biofilm, and water.

21. The method of any one of claims 19 and 20, wherein:

the inorganic nanoparticles are present in the treatment composition in an amount of from 0.001 wt.% to 60 wt.% by total weight of the treatment composition.

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22. The method of claims 19 and 20, wherein:

the inorganic nanoparticles are present in the treatment composition in an amount of from 0.01 wt.% to 10 wt.% inorganic nanoparticles by total weight of the treatment composition.

23. The method of claim 19, further comprising:

passing a pig or body through the pipeline to spread the composition upon surfaces of the interior of the pipeline.

24. The method of claim 20, further comprising:

applying a corrosion inhibitor to the interior surfaces of the pipeline after the composition and materials adhering to the surfaces of the interior of the pipeline are removed.

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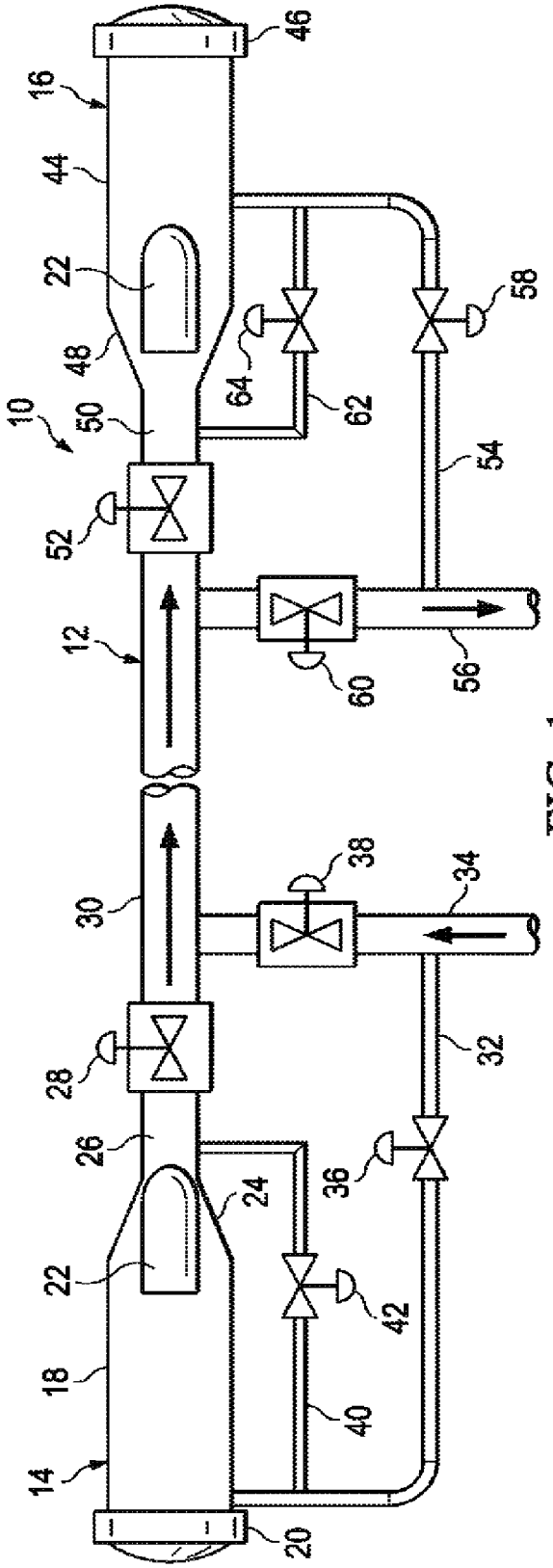


FIG. 1
(PRIOR ART)

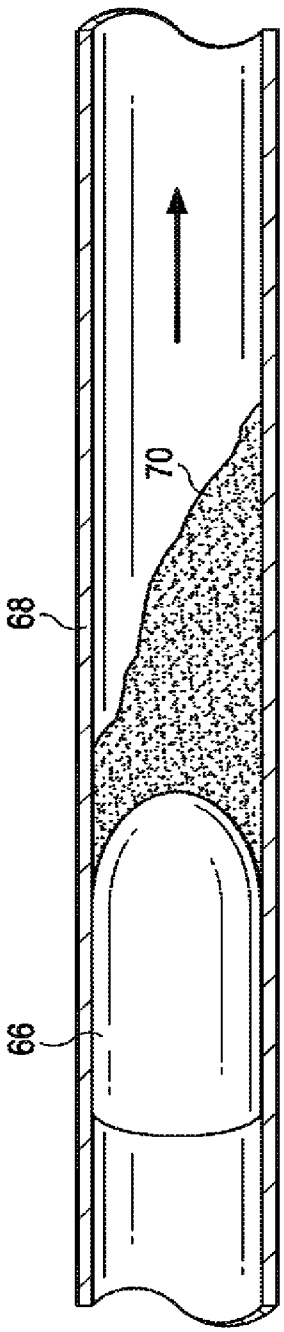


FIG. 2

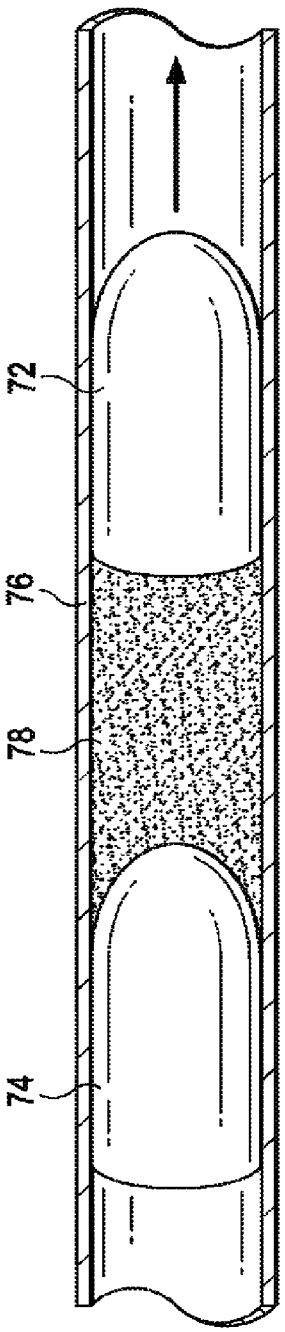
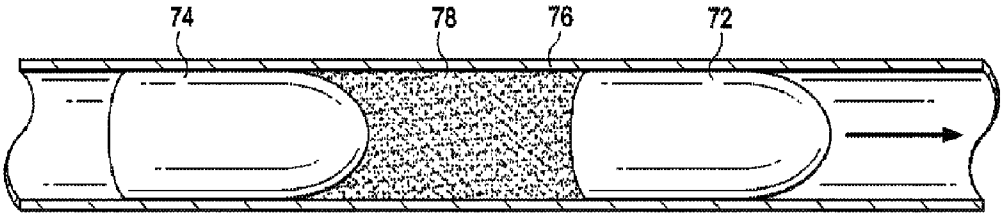


FIG. 3


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